IMPROVED CRYSTAL QUALITY BY DETACHED SOLIDIFICATION IN MICROGRAVITY

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Summary

Many microgravity directional solidification experiments yielded ingots with portions that grew without contacting the ampoule wall, leading to greatly improved crystallographic perfection. Our long term goals have been:

- To develop a complete understanding of all of the phenomena of detached solidification.
- To make it possible to achieve detached solidification reproducibly.
- To increase crystallographic perfection through detached solidification.

We have three major achievements to report here:

- We obtained a new material balance solution for the Moving Meniscus Model of detached solidification. This solution greatly clarifies the physics as well as the roles of the parameters in the system.
- We achieved detached solidification of InSb growing on earth in BN-coated ampoules.
- We performed an extensive series of experiments on freezing water that showed how to form multiple gas bubbles or tubes on the ampoule wall. However, these did not propagate around the wall and lead to fully detached solidification unless the ampoule wall was extremely rough and non-wetted.

Material Balance Solution To The Moving Meniscus Model

Many directional solidification experiments in space yielded ingots with sections that had little or no contact with the ampoule wall [reviewed in 1]. We call this "detached solidification." When detachment occurs, the dislocation density is greatly reduced and grains and twins can no longer nucleate at the ampoule wall. Regel and Wilcox [2] proposed the Moving Meniscus Model shown in Fig. 1 to explain this puzzling phenomenon. There is a gap between the solid and the ampoule wall, while the melt remains in contact with the ampoule. During solidification, the meniscus moves along the ampoule wall at the freezing rate. There must be a pressure difference across the meniscus because of its curvature. This pressure difference is provided by a gas, which is dissolved in the melt at its top surface, rejected by the growing solid, and released across the meniscus into the gap. Based on the Moving Meniscus Model, numerical calculations were performed for InSb [3-6] and for water [7]. Detached solidification was predicted to occur in a sealed ampoule at zero gravity under proper conditions; the gas pressure P_m above the melt must be above a critical value [3,7], the freezing rate V_c must exceed a critical value [3,7], Henry's constant H of the dissolved gas must be below a critical value [7], the temperature of the top of the melt must be below a critical value [7], the contact angle θ of the melt on the ampoule wall and the growth angle α must exceed critical values [4], and the diffusion coefficient D of the gas in the melt must exceed a critical value [3,7]. Each critical value depends on the other physical properties and operating conditions, so that different results were obtained for InSb and water

Keywords: indium antimonide, detached solidification, dewetting

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Supported by NASA's Office of Biological and Physical Research under grant NAG8-1482

[7]. Within the range of parameters predicted to yield steady-state detachment, two solutions were found, one with a large gap and one with a small gap between the solid and the ampoule wall.

As is typical of numerical simulations, a thorough understanding of the factors contributing to the behavior predicted above has been elusive. For that reason we sought to develop an approximate analytical solution. We were encouraged by the observation that although Marangoni convection along the meniscus dramatically alters the velocity and concentration fields, it does not markedly influence detachment [3]. A steady state material balance approach was successful, and does reveal the essential physics [8].

Non-dimensionalization of the governing equations for the Moving Meniscus Model allowed consolidation of the operating conditions and physical properties into five dimensionless parameters. At steady state, the flux of gas dissolved in the melt moving toward the freezing interface must equal the sum of the flux of gas into the gap plus that being incorporated in the growing solid. Both numerical and material balance results give two solutions, with an extremum value of each variable beyond which steady detachment is impossible. This behavior is now understood to originate from satisfaction of the material balance at two different gap widths, with these two solutions becoming identical at an extremum condition beyond which the material balance cannot be satisfied. Only one solution is obtained when no gas is incorporated in the solid. In the presence of gravity, the gas pressure in the gap must be much larger to compensate for the added hydrostatic pressure, causing the gap width to be narrow.

Figure 2 shows the material balance volume used to obtain an approximate analytical solution for steady state detached solidification. The flux N_L of dissolved gas into this volume was found from the freezing rate and the concentration of dissolved gas, which was assumed to be the solubility of residual gas in the melt at the temperature and pressure at the top of the melt. The flux N_G of gas into the gap was obtained from the pressure of gas inside the gap, which was calculated from the curvature of the meniscus, the curvature of the top surface of the melt, and the hydrostatic head (on earth) of the column of melt. The flux N_S was obtained from the equilibrium distribution coefficient of dissolved gas in the solid together with the dissolved gas concentration in the melt along the freezing interface. The concentration field was obtained by an approximate analytical solution of the partial differential equation for diffusion. At steady state, the flux into the volume must equal that out, or $N_L = N_S + N_G$.

Figure 3 shows the three fluxes versus the gap width for a base set of values of the governing parameters. For these conditions, there are two steady state solutions where the curve for $N_S + N_G$ intersects that for N_L. By varying the experimental parameters, the curve for $N_S + N_G$ can be raised so that the two solutions become closer and closer. When the two curves become tangent, there is only one solution. As $N_S + N_G$ is raised still farther, the two curves do not intersect and steady state detachment is impossible.

The computer algebra system Maple was used to find the gap width e versus various parameters. Figure 4 shows a comparison of results predicted from this material balance method to those predicted from numerical solution of the differential equations for the Moving Meniscus Model. At small values of the gap width the agreement is excellent, but the two methods diverge somewhat for large values of the gap width. This reflects the error in the estimate of the dissolved gas concentration along the freezing interface. Nevertheless, both methods show maxima in the values of the parameters that will yield a solution. Figure 4 also confirms the utility of non-dimensionalizing the governing equations, as well as indicating the error in the numerical solution.

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The influence of gravity was also investigated. The added hydrostatic pressure in the gap causes the steady state gap widths to become smaller. Furthermore, detachment is not possible unless the segregation coefficient *k* is small. Convection was not considered here, but may either increase or decrease the flux of gas into the gap, depending on the convection pattern and its vigor [6].

Detached Solidification Of InSb On Earth

Indium antimonide (InSb) has often exhibited detached solidification from microgravity experiments. Here, we directionally solidified InSb on earth using the vertical Bridgman-Stockbarger technique [10]. A pyrolytic boron nitride (BN) coating was formed on the inside of some of the quartz ampoules by reacting a layer of boric acid with ammonia gas. Detachment often occurred, as illustrated in Figures 5, 6 and 7. It was favored by the boron nitride coating, a 10 mm/h growth rate, and 20 kPa of forming gas (10% H_2 in Ar) in the ampoule. The detached portion sometimes completely circled the ingot, and sometimes went only part way around. Tiny facets could be seen on many detached regions. Detachment did not occur at the top or bottom of the ingot, when the ampoule was too short, or when the ingot was oxidized due a leak in the ampoule.

Gas Bubble And Tube Formation In Ice

A vertical Bridgman-Stockbarger apparatus was used to directionally solidify water upward, in the hope that detached solidification would evolve from gas bubbles forming on the wall [9,11]. A large contact angle of the water on the ampoule wall and a high solubility of the dissolved gas caused gas bubbles or tubes to form only at the ampoule wall, and not in the interior. Gas tubes were often nearly periodically spaced around the ampoule wall (e.g., Figure 8), with a spacing that increased with ampoule diameter and decreased with freezing rate. The width of the gas tubes was nearly independent of the ampoule diameter and freezing rate. A high degree of detachment was obtained with a rough, non-wetting coating on the ampoule wall, but full detachment was not achieved. This indicates that detachment does not occur by propagation of a single gas bubble around the periphery of the freezing interface. The convection near the freezing interface influenced gas bubble formation, and was outward for a concave freezing interface and inward for a convex interface.

Similar semi-periodic gas tubes were produced in freezing of zone-refined naphthalene [12].

Acknowledgement

The InSb used for these experiments was kindly donated by Firebird Semiconductors Ltd., Trail, BC, Canada V1R 2T3.

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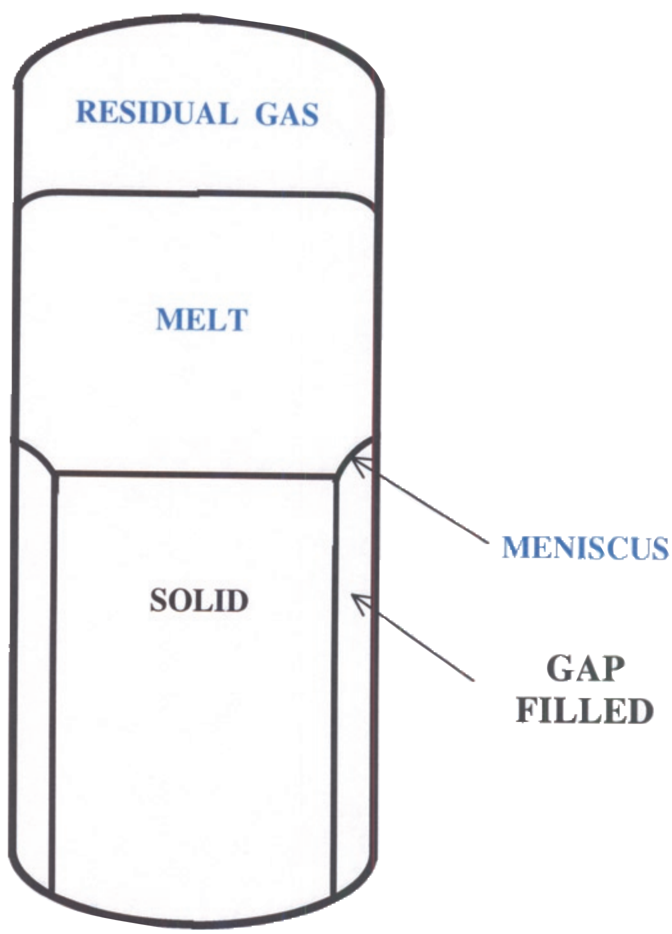

Figure 1. Schematic diagram of the Moving Meniscus Model for Detached Solidification.

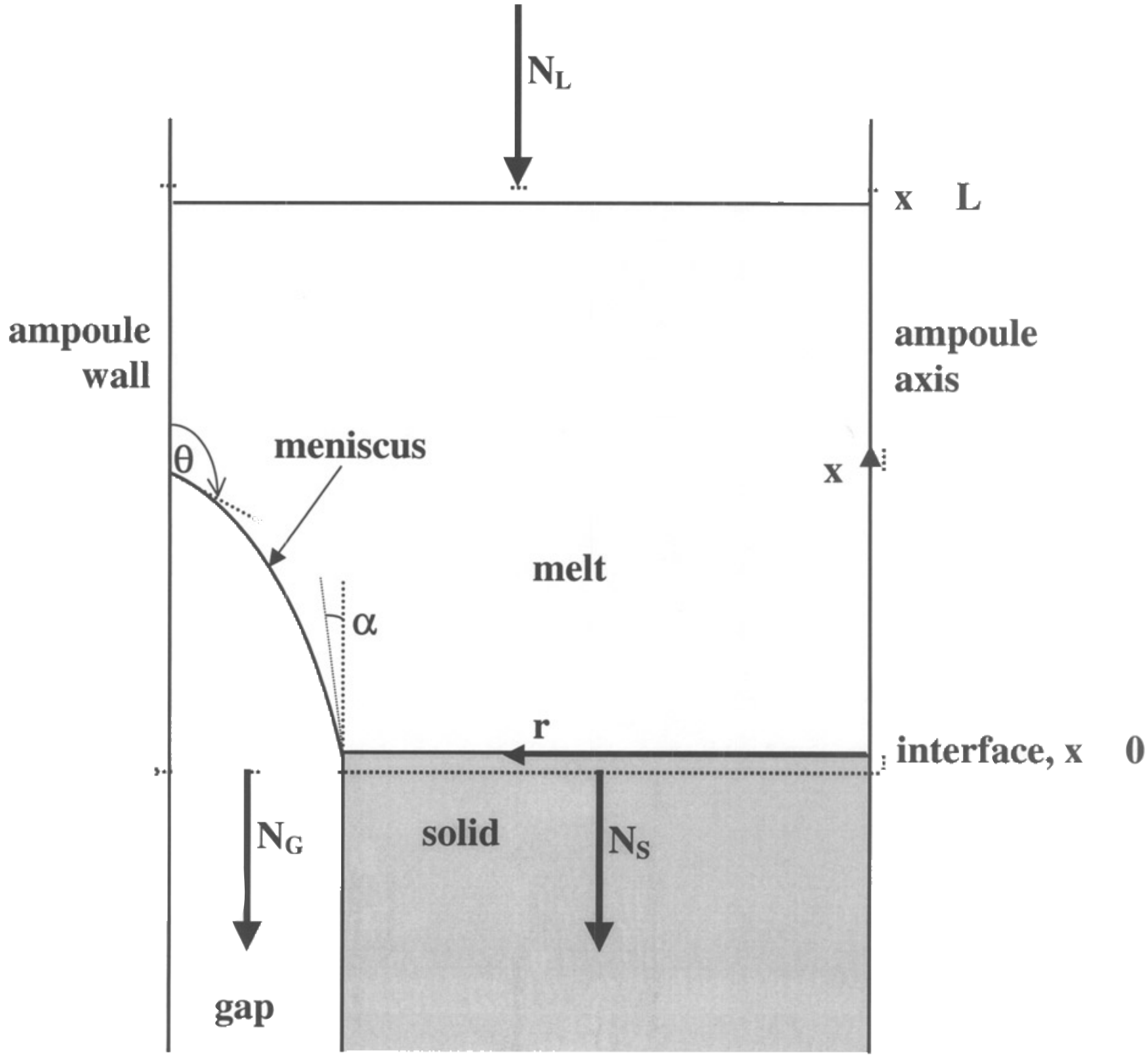

Figure 2. The material balance volume is indicated by the dotted line. Here, N_S is the flux of dissolved gas into the freezing solid, N_G is the flux of gas into the gap, N_L is the flux of dissolved gas carried by the melt entering the volume, θ is the contact angle of the melt on the ampoule wall, and α is the growth angle. At steady state, the flux into the volume must equal that out, or $N_L = N_S + N_G$. The length L of the liquid column is chosen long enough such that it is beyond the region near the freezing interface where the concentration of dissolved gas varies.

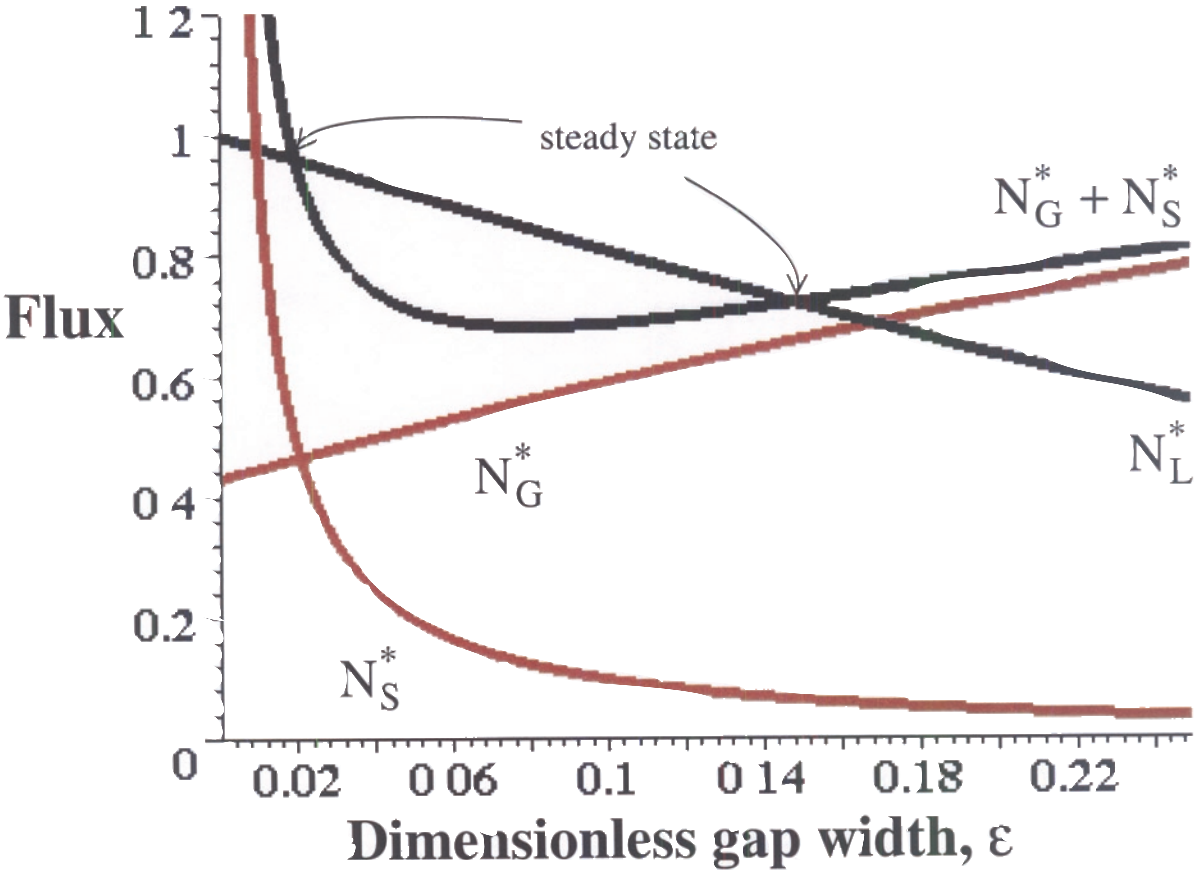

Figure 3. Dimensionless fluxes of dissolved gas versus gap width for base conditions at zero gravity. The fluxes were non-dimensionalized by dividing by the flux of dissolved gas coming in with the melt when there is no gap. The gap width e was non-dimensionalized by dividing by the ampoule radius. For the conditions used to calculate the results shown above, there are two steady state solutions where the curve for $N_S + N_G$ intersects that for N_L. By varying the experimental parameters, the curve for $N_S + N_G$ can be raised so that the two solutions become closer and closer. When the two curves become tangent, there is only one solution. As $N_S + N_G$ is raised still farther, the two curves do not intersect and steady state detachment is impossible.

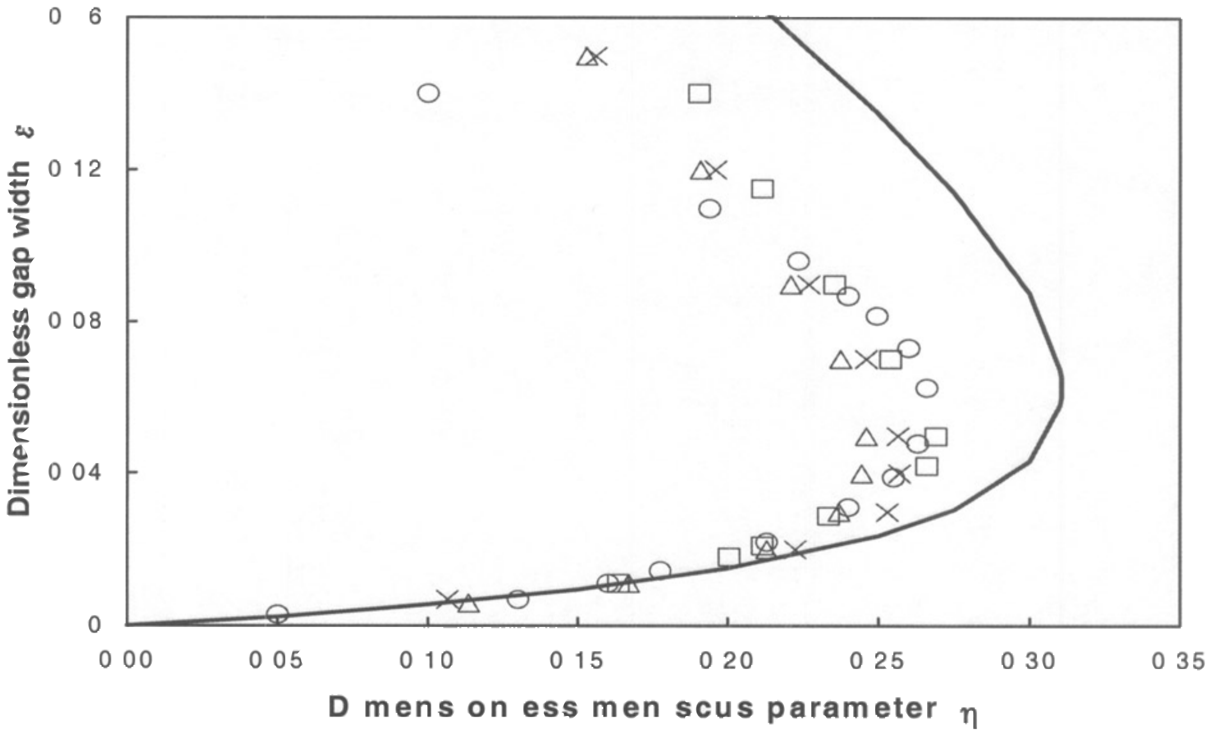

Figure 4. Comparison of the material balance solution with results from numerical solutions of the Moving Meniscus Model for the limiting case of very large ampoule with different parameters held constant.

——— Material balance

×	Numerical for σ varied	○	Numerical for η varied
□	Numerical for P_m varied	△	Numerical for θ varied

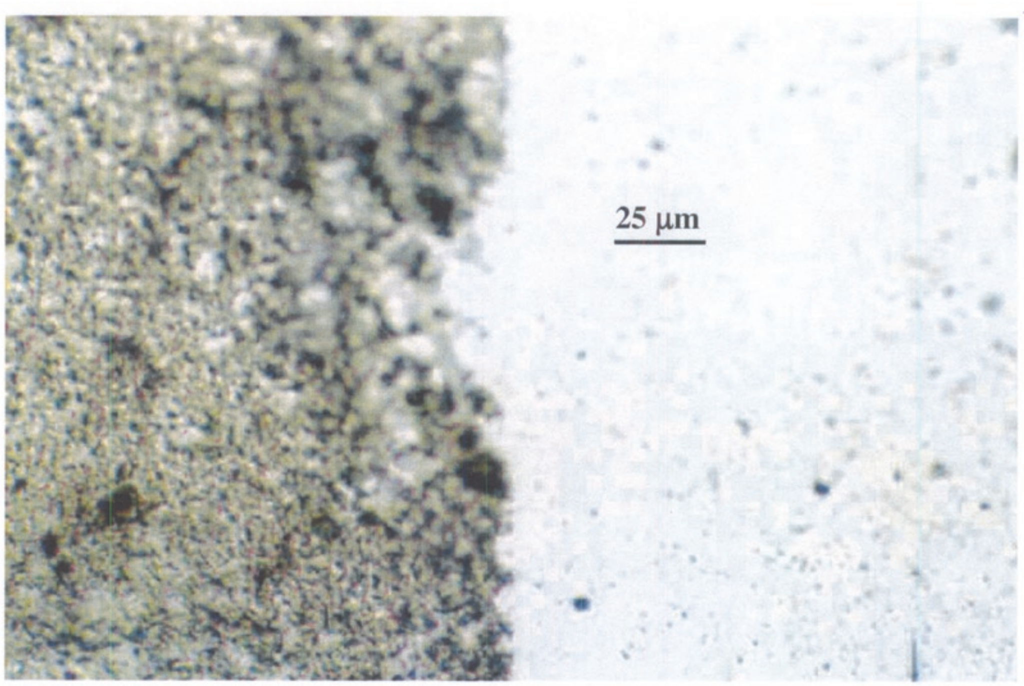

Figure 5. Close-up of boundary between detached and detached sections of ingot 6. Taken at 400 X.

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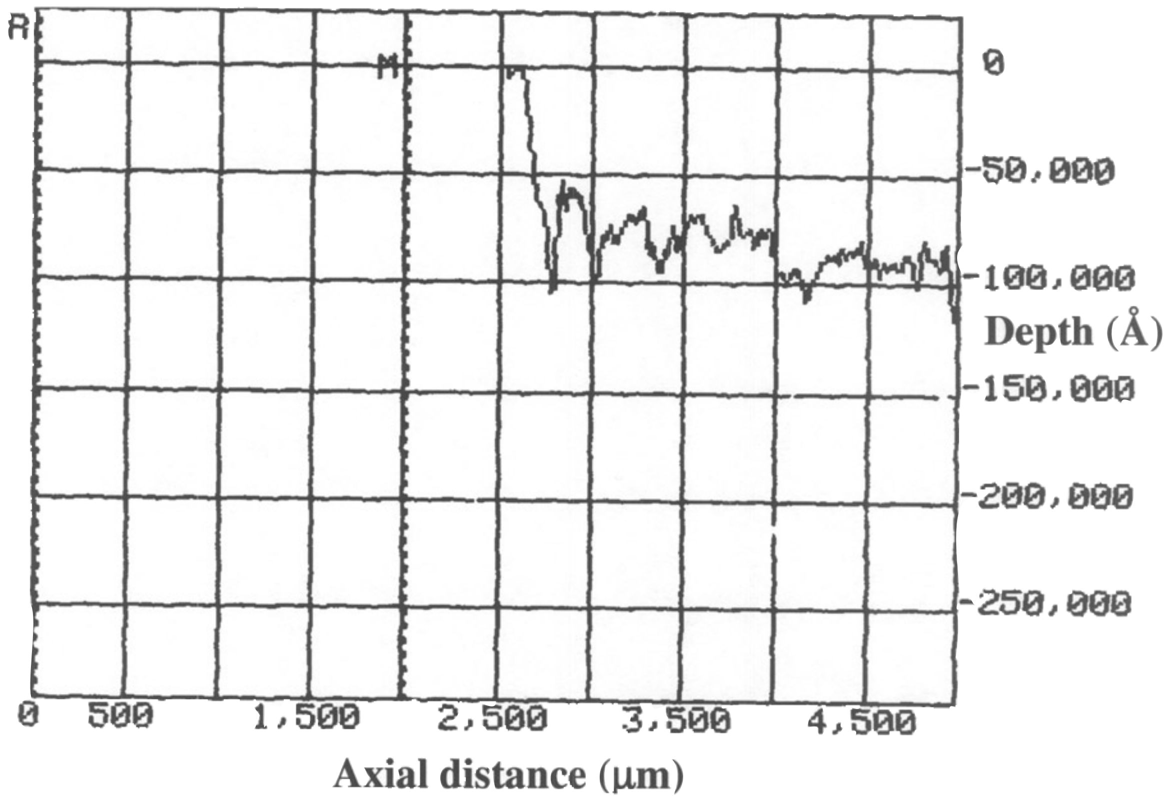

Figure 6. Topography of ingot 6 via profilometer scan lengthwise along the surface.

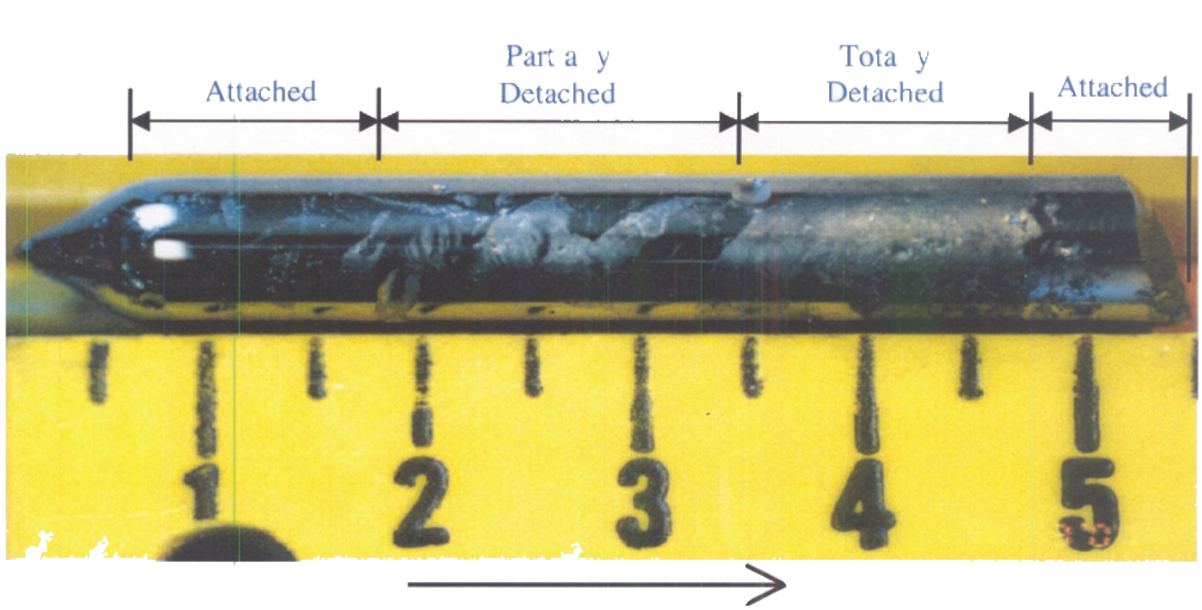

Figure 7. Photograph of Ingot 6. Scale is in cm. The arrow indicates the growth direction. Growth conditions are: BN-coated ampoule, 10 mm/h freezing rate, 50 kPa of forming gas inside the growth ampoule. "Totally Detached" indicates that the entire circumference grew without contacting the ampoule, while "Partially Detached" indicates that detachment only went part way around.

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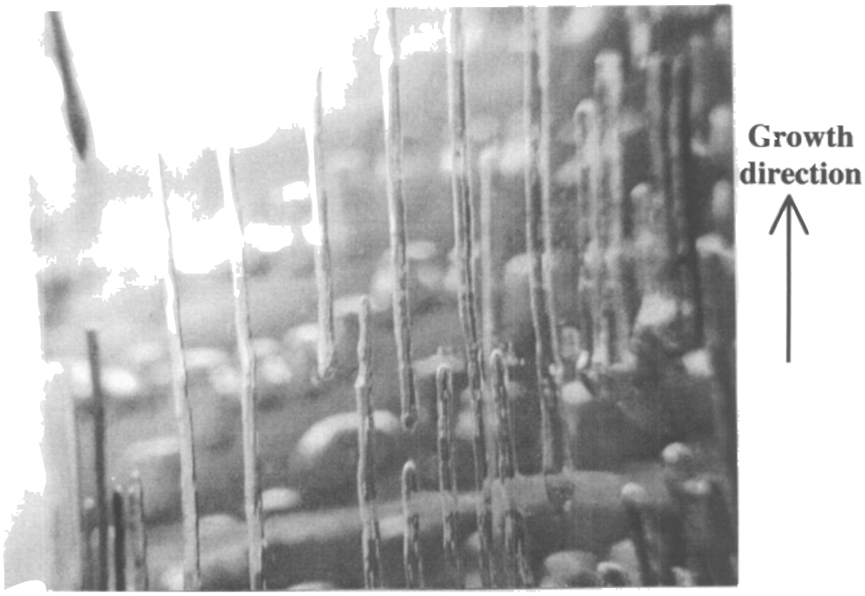

Figure 8. Roughly periodic gas tubes formed on the ampoule wall with a freezing rate of 12 mm/h. The water was saturated with air and the 10 mm inside diameter ampoule was coated with Teflon. Sample width ~10 mm

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